

Supplementary information for:

Membrane reinforcement in Giant Hybrid Polymer Lipid Vesicle achieved by controlling the polymer architecture

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Brief recall of the synthesis procedure of the copolymers, published in ^{1,2}

Synthesis of triblock copolymers²

The amphiphilic triblock copolymers PEO₈-*b*-PDMS₂₂-*b*-PEO₈ and PEO₁₂-*b*-PDMS₄₃-*b*-PEO₁₂ were synthesized via coupling of two hydrophilic PEO blocks onto a hydrophobic PDMS block. Hydrophobic blocks were the α,ω -bisaminopropyl-terminated poly(dimethylsiloxane) (NH₂-PDMS-NH₂) with a number average molecular weight of 1500 and 3000 g.mol⁻¹ according to the provider's data (ABCR, Germany) and as also verified by ¹H NMR, defining 22, and 43 units for PDMS chain respectively. Succinimidyl-((N-methyl)-ethyleneglycol) ester (509 and 685.7 g/mol) or (PEO-NHS) corresponding to 8 and 12 units of PEO chain) were used as hydrophilic blocks, purchased from Thermo Fisher Scientific Inc. The coupling reactions were carried out under an inert gas in dichloromethane with the presence of DIPEA during 24h at room temperature. The obtained products were then purified by dialysis using a membrane with MWCO of 50kDa. The copolymer was characterized by ¹H NMR in CDCl₃ and Size Exclusion Chromatography in THF.

Synthesis of diblock copolymers¹

All The diblock copolymers PDMS-*b*-PEO in this study were synthesized by ring-opening polymerization of a cyclic siloxane monomer (D₃), functionalization of the PDMS chain and further coupling with alkyne end-functionalized poly(ethylene oxide) using Huisgen's coupling. For that, hexamethylcyclotrisiloxane, dried over CaH₂ and dissolved in freshly distilled THF, was polymerized under argon using butyllithium in cyclohexane/hexane. The solution was stirred at room temperature for 2 h then the reaction was quenched by adding chloro-(3-chloropropyl)dimethylsilane. After filtration, washing in methanol and further drying process the polymer was characterized by ¹H NMR, SEC in toluene, and FT-IR. Then, the end-chain was functionalized with an azido group by addition of NaN₃ into a solution of PDMS-Cl in dimethoxyethane and dimethylformamide (50/50 vol./vol.). After dilution in pentane and washing procedure with water, the solvent was evaporated and product was dried under vacuum before characterization by ¹H NMR, SEC in toluene and FT-IR.

A commercial methoxy terminated PEO dissolved in freshly distilled THF was reduced by NaH and functionalized by addition of a solution of propargyl bromide at 80 wt.% in toluene. After 24 h, the mixture was concentrated, then diluted in dichloromethane and washed with water. After a drying, the final product was characterized by ¹H NMR and SEC in THF.

Finally, azido functionalized PDMS was then coupled to alkyne functionalized PEO in toluene. PMDETA and CuBr were added and reaction was conducted at 80°C for 24 h. The solvent was then evaporated and the product was solubilized in dichloromethane and purified on silica column using a 7 vol.% mix of methanol with dichloromethane as eluent phase. The product was dried under vacuum overnight and the final product was characterized by ^1H NMR and SEC in THF.

Influence of fluorescent probe on mechanical properties of GUV

We have evaluated the potential influence of the fluorescent probes used for confocal imaging, on the mechanical properties of GUV.

For that we have studied the behaviour of giant polymersomes obtained from the self-assembly of $\text{Si}_{27}\text{EO}_{17}$, without fluorescent probe, with 2% of PDMS-NBD, and in a last case with 0.2% of PE Rhodamine. We have also studied mechanical properties of GHUV without probes, with 0.2% of PE rhodamine and with both probe 0.2% PEI rhodamine and 2% PDMS-b-NBD. The profile of the membrane tension versus the area expansion is represented for the different systems in the Figure S3.

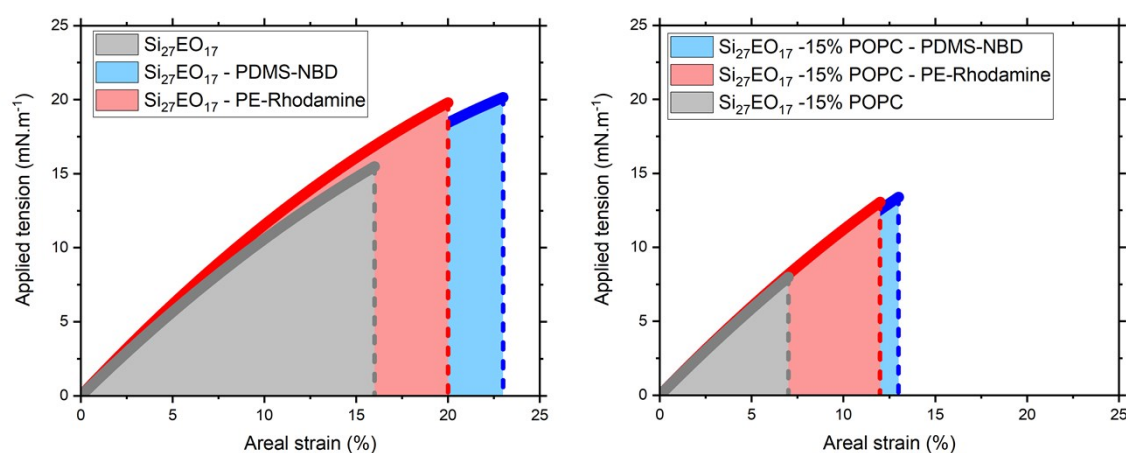


Figure S1 left: Membrane tension versus area expansion for the polymersomes with different probes. Right B Same thing for GHUV (15% POPC) with different probes.

It is clear from the results obtained that the presence of probes in the membrane has an influence on the mechanical properties. If the stretching moduli are almost unchanged, the Lysis strain is modulated and can be higher or lower than the lysis strain of the pure polymersomes or GHUV. We do not have clear explanation of this experimental fact. All the mechanical properties of the GHUV in this article were analyzed without fluorescent probes.

Appearance of polymer aggregation for the $\text{Si}_{36}\text{EO}_{23}$ /POPC system

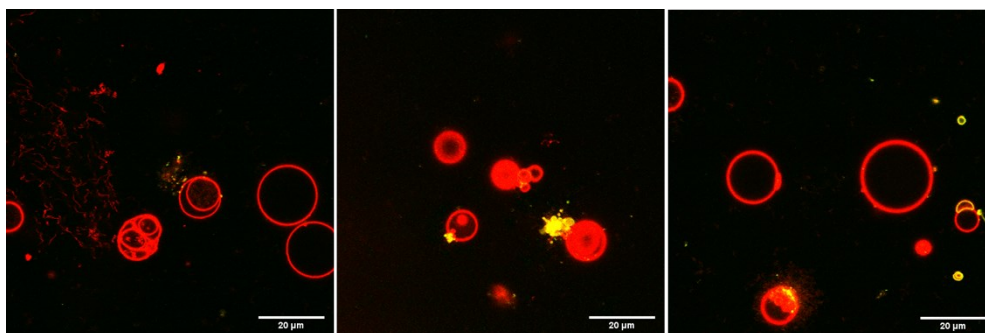


Figure S2 – Confocal images showing the aggregation of the $\text{Si}_{36}\text{EO}_{23}$ on membranes formed by POPC when the lipid fraction is above 40 wt.% in the initial mixture.

Mechanical properties measurements

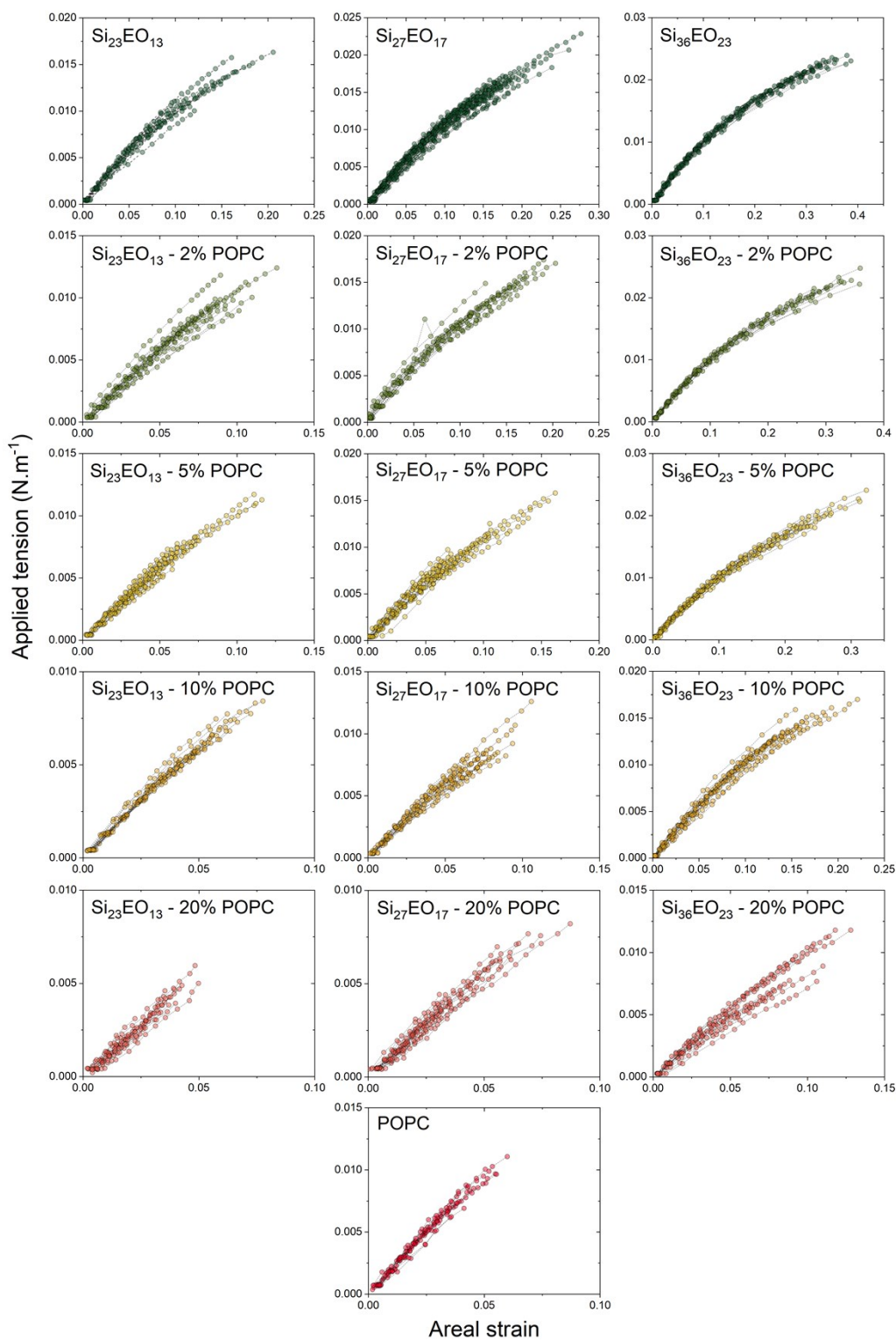


Figure S3 - Stress strain curves of GHUVs prepared from Si₂₃EO₁₃, Si₂₇EO₁₇ and Si₃₆EO₂₃ at different POPC fractions.

Table S1: Mechanical properties of Hybrid vesicle's membranes

	POPC fraction (wt.%)	Stretching modulus (mN.m ⁻¹)	Lysis strain (%)	Lysis stress (mN.m ⁻¹)	Toughness (mN.m ⁻¹)
Si₂₃EO₁₃	0	118 ± 10	12 ± 4	12 ± 3	0,87 ± 0,50
	2	122 ± 12	9 ± 2	10 ± 1	0,46 ± 0,15
	5	122 ± 11	7 ± 3	8 ± 2	0,30 ± 0,21
	10	130 ± 10	5 ± 1	6 ± 1	0,18 ± 0,09
	20	118 ± 13	3 ± 1	4 ± 1	0,06 ± 0,03
Si₂₇EO₁₇	0	121 ± 8	16 ± 4	15 ± 3	1,37 ± 0,67
	2	120 ± 10	15 ± 3	14 ± 2	1,24 ± 0,44
	5	132 ± 13	9 ± 4	10 ± 3	0,50 ± 0,38
	10	125 ± 12	7 ± 2	8 ± 2	0,32 ± 0,15
	20	121 ± 14	5 ± 2	5 ± 2	0,14 ± 0,10
Si₃₆EO₂₃	0	113 ± 3	32 ± 5	22 ± 2	4,20 ± 1,06
	2	112 ± 3	29 ± 6	21 ± 3	3,63 ± 1,12
	5	114 ± 4	24 ± 5	19 ± 3	2,71 ± 1,00
	10	116 ± 7	15 ± 3	14 ± 2	1,17 ± 0,40
	20	105 ± 11	8 ± 3	8 ± 3	0,38 ± 0,24
POPC	100	204 ± 13	4 ± 1	8 ± 2	0,17 ± 0,09

(1) Fauquignon, M.; Ibarboure, E.; Carlotti, S.; Brûlet, A.; Schmutz, M.; Le Meins, J.-F. *Polymers* **2019**, *11*, 2013.

(2) Dao, T. P. T.; Brûlet, A.; Fernandes, F.; Er-Rafik, M.; Ferji, K.; Schweins, R.; Chapel, J. P.; Fedorov, A.; Schmutz, M.; Prieto, M.; Sandre, O.; Le Meins, J. F. *Langmuir* **2017**, *33*, 1705.